

Kinetics of Oxidation of 2,6-Dimethylphenol (DMP) Using Novel μ -Carbonato $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ Complexes

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Abstract

This paper reports the kinetics of the oxidation of 2,6-dimethylphenol (DMP) to get 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (DPQ) using novel oxidative coupling complexes $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ ($n = 1$ or 2 , $X = \text{Cl}$ or Br , $\text{Pip} = \text{piperidine}$). The new prepared tetranuclear complexes were characterized using cryoscopic measurements, electronic spectra, FTIR, EPR and cyclic voltammetry techniques. These complexes are catalytically active. The proposed mechanism of the catalytic oxidative coupling can be illustrated as a pre-equilibrium, K , between the catalyst and DMP to form a complex intermediate which is converted to activated complex through the rate determining step, k_2 , to form the final product. The inverse of the observed rate constants k_{obsd} versus $1/[\text{DMP}]^2$ gives a straight line with intercept. From the slope and the intercept, both K and k_2 are obtained. At different temperatures, thermodynamic and kinetic parameters are evaluated. It is worth to mention that, the dependence of k_{obsd} on $[\text{DMP}]^2$ indicates that the coordination number for every copper center in both $n = 1$ or 2 in $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ is equal to six. Therefore, carbonato bridging centers in $n = 1$ acts as a tridentate ligand, while for $n = 2$ acts as a bidentate ligand.

Keywords

Catalysts, Kinetics, Thermodynamic, Copper Complexes

1. Introduction

The study of homogenous oxidative coupling of DMP using copper catalysts has attracted scientists for several

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years from the catalytic industry point of view as well as a model for tyrosinase enzyme. These copper catalysts showed activity towards phenol oxidation like tyrosinase [1]-[13]. In previous work it was reported that the oxo copper complexes showed a catalytic activity towards phenol oxidation [14]-[18]. The full 3D-molecular structure of tetranuclear copper (I) complex of [(Pip)CuI]₄ was studied by Volker Schramm [19] and also the crystal structure of the copper (I) iodide-pyridine was previously reported [20].

The aim of this work is to study the kinetics of oxidation of DMP to DPQ (Scheme 1) using the prepared [(Pip)_{4n}Cu₄X₄(CO₃)₂] complexes and the strategy is:

1) The use of well investigated tetranuclear carbonato-copper (II) complexes, [(Pip)_{4n}Cu₄X₄(CO₃)₂] as catalysts for oxidation of (DMP) to (DPQ).

2) To evaluate those initiators [(Pip)_{4n}Cu₄X₄(CO₃)₂] with [(Pip)_{4n}Cu₄X₄O₂], the mechanism will deal with the first cycle under dinitrogen and the reaction followed by reduction of copper (II) to copper (I) at 740 nm or by DPQ formation at 431 nm.

3) The efficiency of the [(Pip)_{4n}Cu₄X₄(CO₃)₂] relative to the oxo analogues for oxidative coupling of (DMP) to (DPQ).

4) The impact of structural change in [(Pip)_{4n}Cu₄X₄(CO₃)₂] when n changes from 1 to 2, since the maximum coordination number of copper (II) is six.

2. Experimental

2.1. Reagents

Piperidine, Pip (Aldrich) was used as received. 10 cm column of Drierite was utilized to dry CO₂ gas. The copper (I) halides as well as C₆H₅NO₂, CH₂Cl₂, DMP and N₂ gas were prepared for this work according to the procedures described in the literature [21].

2.2. Instrumentation

The rates of oxidation of (DMP) by copper complexes [(Pip)_{4n}Cu₄X₄(CO₃)₂]; in C₆H₅NO₂ were measured by 160 A uv-visible recording spectrophotometer Shimadzu in matched quartz cells. The monitoring wavelength was 740 nm. Activation parameters were elucidated by repeating the reactions at different temperatures (20°C - 50°C). All reactions and measurements are carried out at least three times under fixed conditions to give maximum error of ±4% in each reported rate constant.

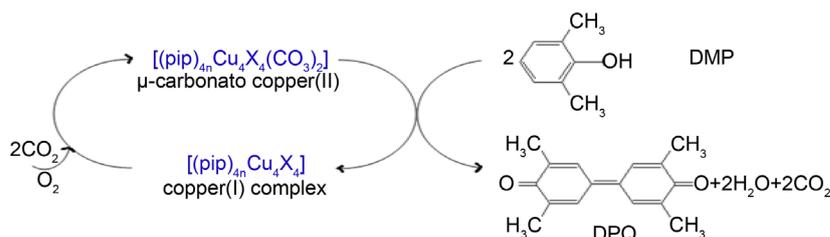
2.3. Kinetic Measurements

The mechanism and kinetics of the catalytic oxidation of DMP (2.0 - 16.0) × 10⁻² M using the copper [(Pip)_{4n}Cu₄X₄(CO₃)₂] complexes (1.0 × 10⁻³ M) in C₆H₅NO₂ were investigated by uv-vis spectrophotometer at 740 nm. Activation parameters were elucidated by repeating the reactions at different temperatures (20°C - 50°C). All reactions and measurements are carried out at least three times under fixed conditions to give maximum error of ±4% in each reported rate constant.

3. Results and Discussion

3.1. Stoichiometry and Products of Oxidation of Copper (I) Complexes by O₂ and CO₂

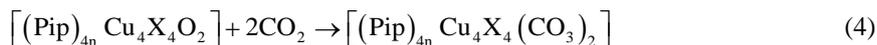
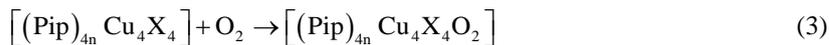
The formation of tetranuclear complexes [(Pip)_{4n}Cu₄X₄]; n = 1 or 2, X = Cl, Br or I under N₂ in C₆H₅NO₂ or CH₂Cl₂ as aprotic solvents were carried out as described in Equation (1) and Equation (2).



Scheme 1. Proposed catalytic cycle for homogenous oxidative coupling of phenols.



The preparation of the new μ -carbonato complexes $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ was performed under N_2 by the reaction of $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4]$ ($n = 1$ or 2) with O_2 followed by fast reaction with CO_2 as described in Equation (3) and Equation (4) and **Scheme 1** [22]-[28].



The μ -carbonato $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ complexes are easily soluble in $\text{C}_6\text{H}_5\text{NO}_2$ and CH_2Cl_2 . The molar mass determination, analytical data, FTIR and electronic spectra (**Figure 1**) indicate that the formed complexes, $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ are stable tetranuclear, similar to their copper (I) precursors (**Scheme 2**) [22]-[28].

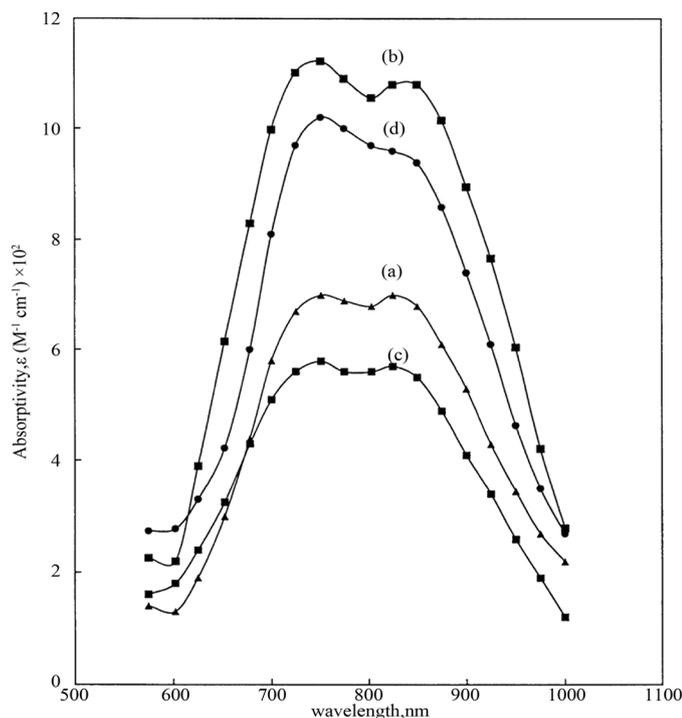
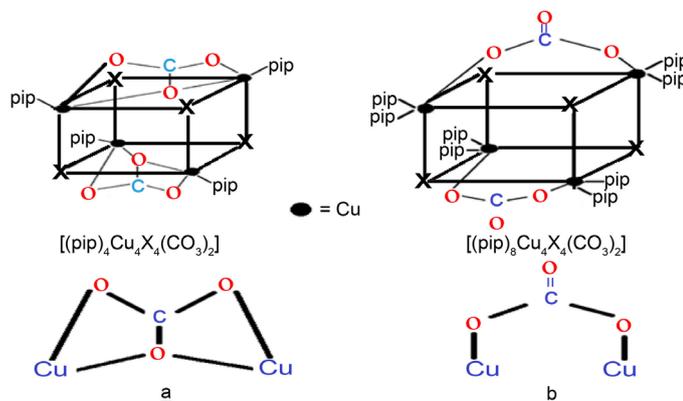


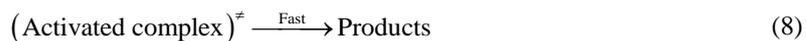
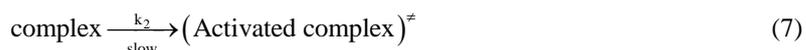
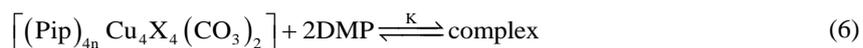
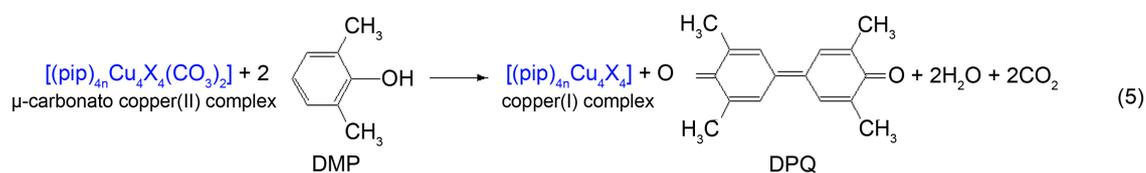
Figure 1. Electronic spectra of (a) $[(\text{Pip})_4\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, (b) $[(\text{Pip})_4\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, (c) $[(\text{Pip})_8\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, (d) $[(\text{Pip})_8\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$.



Scheme 2. Proposed molecular structures for $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$.

3.2. Kinetics of Oxidation of DMP to DPQ Using Novel $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ Complexes

The kinetics of homogeneous oxidative coupling of DMP to DPQ, Equation (5) are investigated at $\lambda_{\text{max}} = 740$ nm under pseudo 1st order conditions, where the concentration of $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ complex is 1.0×10^{-3} M while the excess DMP concentration changes from 2×10^{-2} to 16×10^{-2} M in $\text{C}_6\text{H}_5\text{NO}_2$ under N_2 atmosphere to insure one cycle only, **Figures 2-5**. The first-order plots of $\ln \frac{A_0 - A_\infty}{A_t - A_\infty}$ with time t , where A_t is the absorbance of $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$ at time t , were linear for at least 4 half-lives, **Figures 6-9**. A plot of the reciprocal of the observed pseudo first-order rate constant $1/k_{\text{obsd}}$ vs. $1/[\text{DMP}]^2$ at constant temperature gives a straight line, **Figures 10-13**, suggesting that 2 molecules of (DMP) are included in the rate determining step with 1 molecule of $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$. Such results suggest a mechanism similar to that reported for oxo complexes $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4\text{O}_2]$ (**Scheme 1**), Equations (6)-(10) [29] [30]. From the relation of $1/k_{\text{obsd}}$ vs. $1/[\text{DMP}]^2$, K and k_2 are collected in **Table 1**. Thermodynamic and activation parameters associated with K and k_2 respectively are shown in **Figures 10-13**, **Table 1**.



$$k_{\text{obsd}} = \frac{Kk_2[\text{DMP}]^2}{1 + K[\text{DMP}]^2} \quad (9)$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_2} + \frac{1}{Kk_2[\text{DMP}]^2} \quad (10)$$

3.3. Thermodynamics of the Oxidation of DMP to DPQ

On changing X from Cl to Br in $[(\text{Pip})_{4n}\text{Cu}_4\text{X}_4(\text{CO}_3)_2]$; $n = 1$ or 2 , k_2 and K are increased and both ΔH° and ΔS° are directed to a more favourable reaction (**Table 1**) indicating that reduction of copper (II) is involved in the

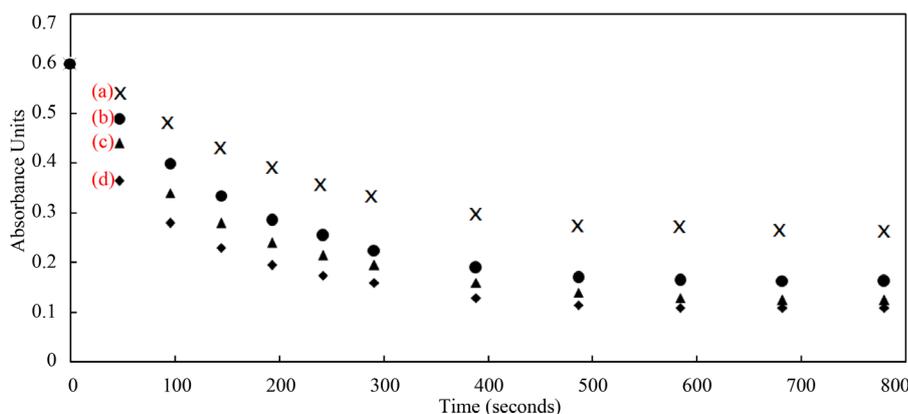


Figure 2. Absorbance-time data for the reaction of $[(\text{Pip})_4\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M with 2,6-dimethylphenol; (a, x) 5.0×10^{-2} M, (b, ●) 7.1×10^{-2} M, (c, ▲) 9.1×10^{-2} M, (d, ◆) 13.8×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C . Monitoring wavelength is 740 nm.

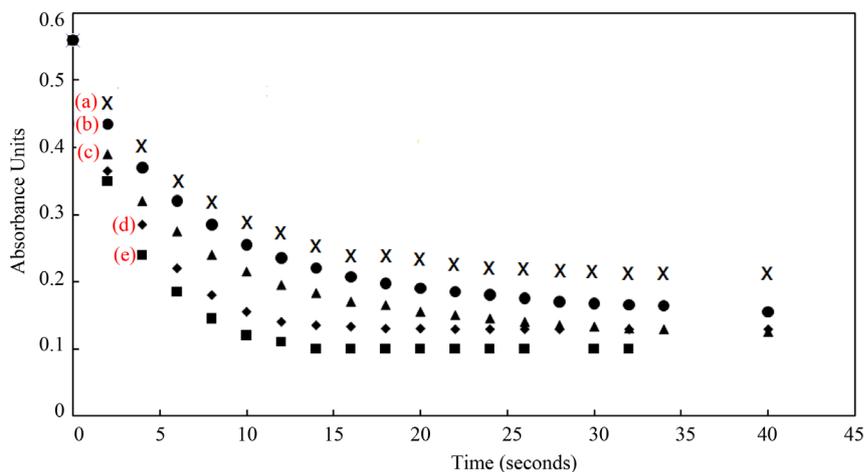


Figure 3. Absorbance-time data for the reaction of $[(\text{Pip})_4\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M with 2,6-dimethylphenol; (a, \times) 2.0×10^{-2} M, (b, \bullet) 3.8×10^{-2} M, (c, \blacktriangle) 5.2×10^{-2} M, (d, \blacklozenge) 8.0×10^{-2} M, (e, \blacksquare) 10.8×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 22°C . Monitoring wavelength is 740 nm.

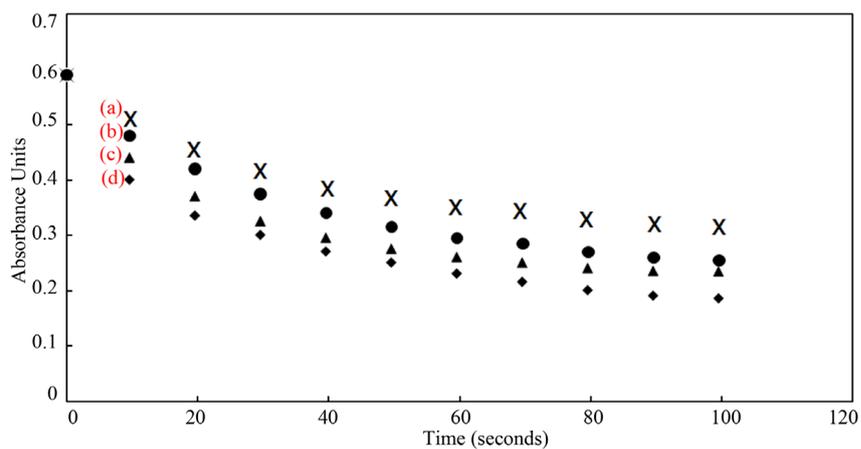


Figure 4. Absorbance-time data for the reaction of $[(\text{Pip})_8\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M with 2,6-dimethylphenol; (a, \times) 5.0×10^{-2} M, (b, \bullet) 6.4×10^{-2} M, (c, \blacktriangle) 9.6×10^{-2} M, (d, \blacklozenge) 16.0×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C . Monitoring wavelength is 740 nm.

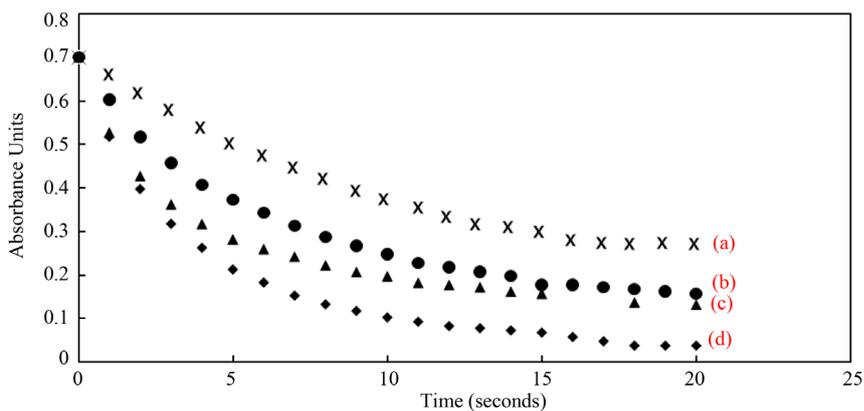


Figure 5. Absorbance-time data for the reaction of $[(\text{Pip})_8\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M with 2,6-dimethylphenol; (a, \times) 2.5×10^{-2} M, (b, \bullet) 5.4×10^{-2} M, (c, \blacktriangle) 6.9×10^{-2} M, (d, \blacklozenge) 9.4×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C . Monitoring wavelength is 740 nm.

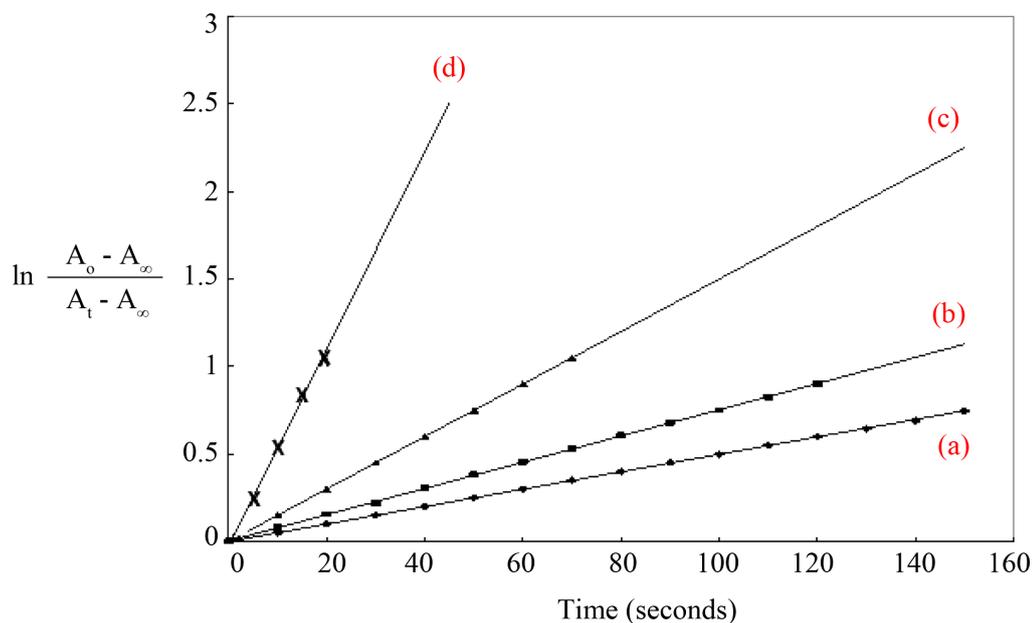


Figure 6. First order plots for the reaction of $[(\text{Pip})_4\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, with 2,6-dimethylphenol, 9.0×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 24°C (a, ♦), 32°C (b, ■), 38°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.

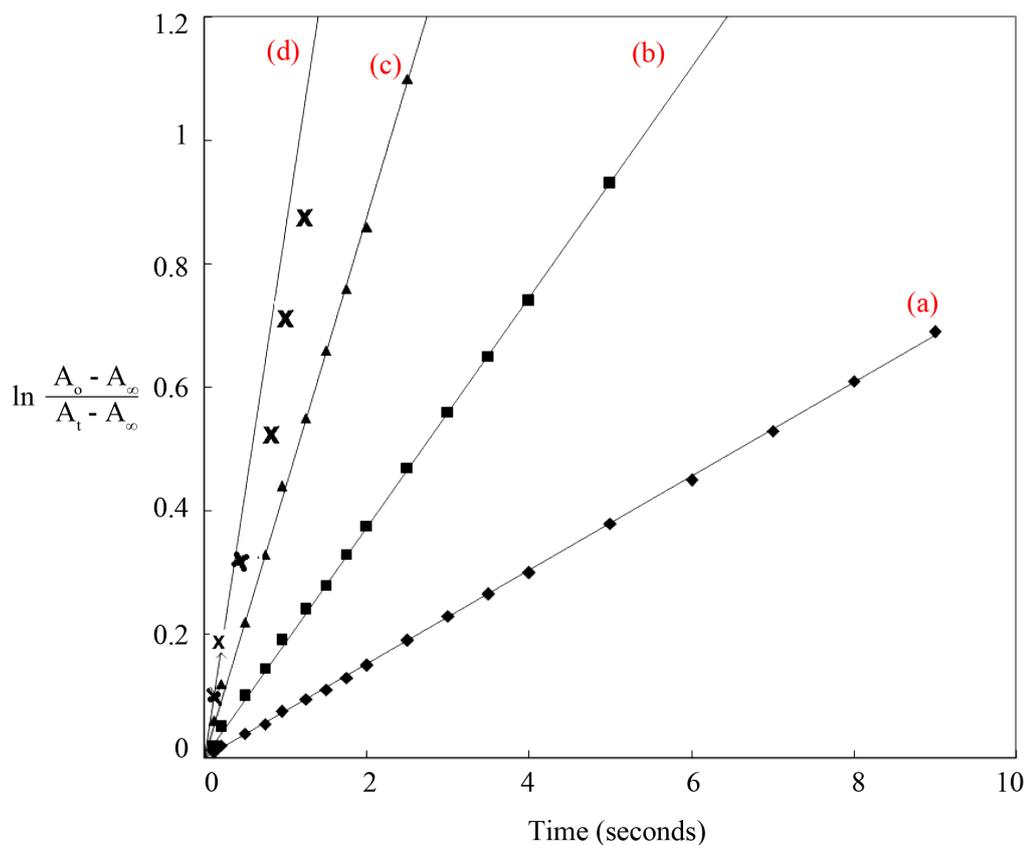


Figure 7. First order plots for the reaction of $[(\text{Pip})_4\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, with 2,6-dimethylphenol, 7.8×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 22°C (a, ♦), 28°C (b, ■), 36°C (c, ▲) and 45°C (d, ×). Monitoring wavelength is 740 nm.

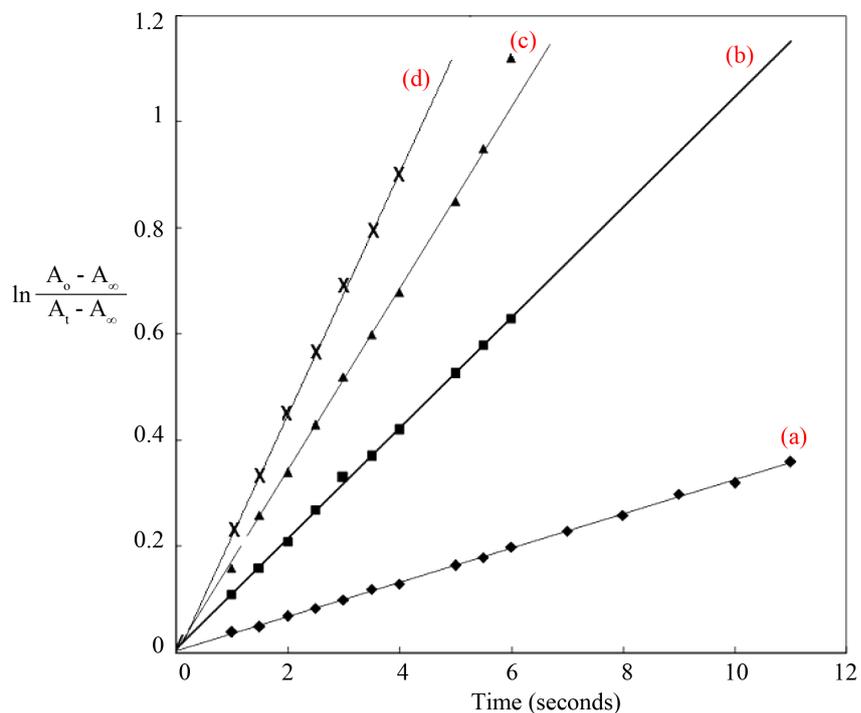


Figure 8. First order plots for the reaction of $[(\text{Pip})_8\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, with 2,6-dimethylphenol, 9.6×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C (a, \blacklozenge), 38°C (b, \blacksquare), 45°C (c, \blacktriangle) and 50°C (d, \times). Monitoring wavelength is 740 nm.

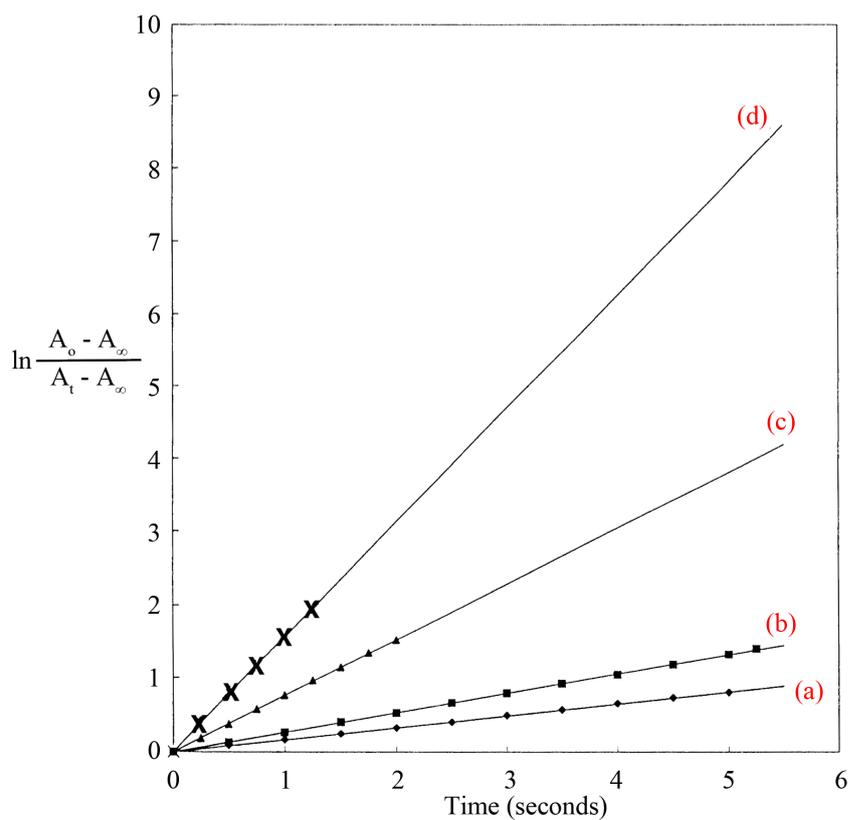


Figure 9. First order plots for the reaction of $[(\text{Pip})_8\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, with 2,6-dimethylphenol, 9.4×10^{-2} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 20°C (a, \blacklozenge), 25°C (b, \blacksquare), 40°C (c, \blacktriangle) and 50°C (d, \times). Monitoring wavelength is 740 nm.

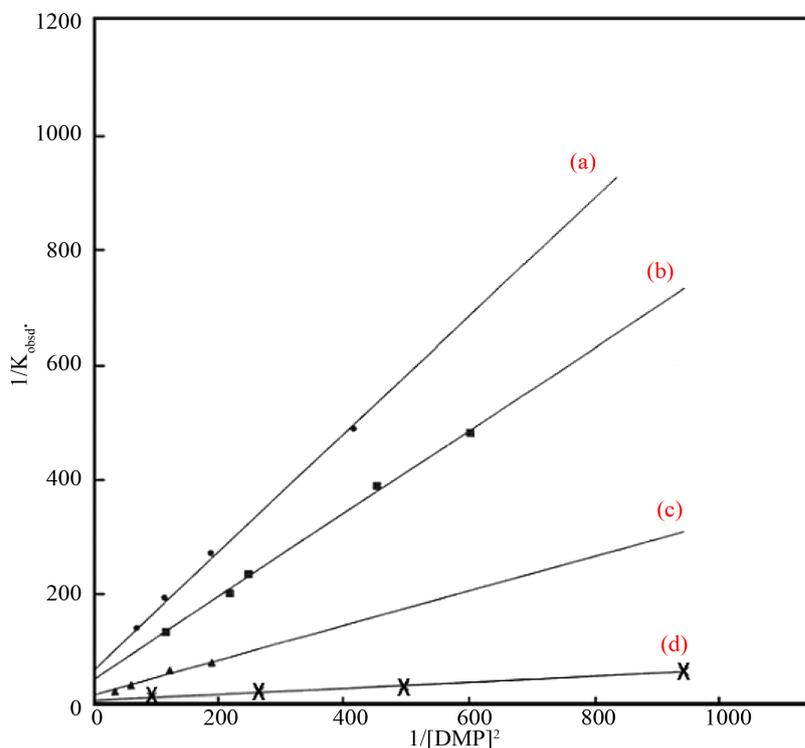


Figure 10. Dependence of the observed pseudo-first order rate constant ($1/k_{\text{obsd}}$) on the $\{1/[DMP]^2\}$ for the reaction with $[(\text{Pip})_4\text{-Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C (a, ●), 32°C (b, ■), 38°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.

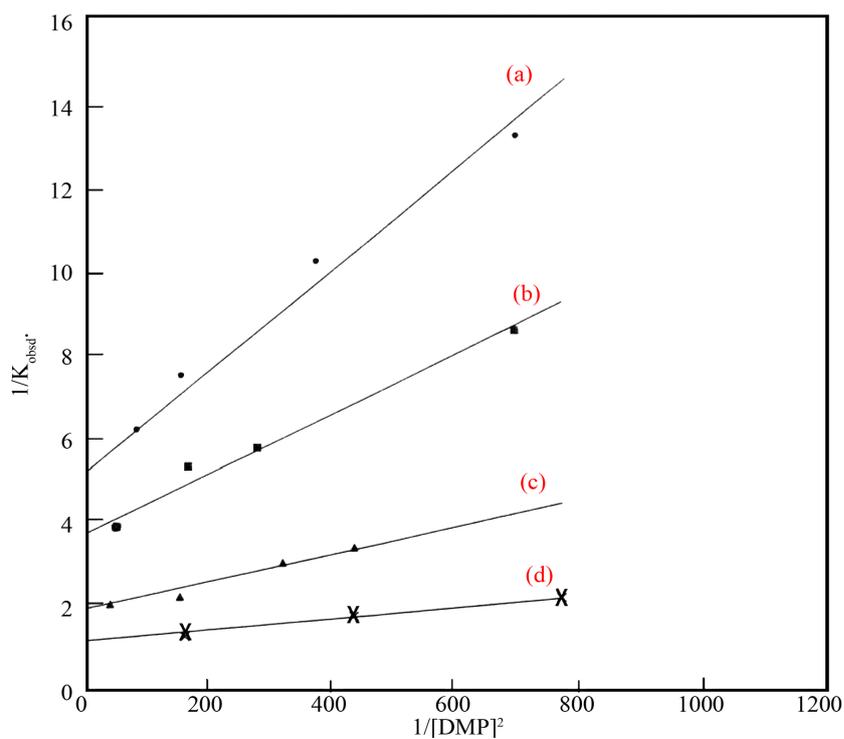


Figure 11. Dependence of the observed pseudo-first order rate constant ($1/k_{\text{obsd}}$) on the $\{1/[DMP]^2\}$ for the reaction with $[(\text{Pip})_4\text{-Cu}_4\text{Br}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 22°C (a, ●), 28°C (b, ■), 36°C (c, ▲) and 45°C (d, ×). Monitoring wavelength is 740 nm.

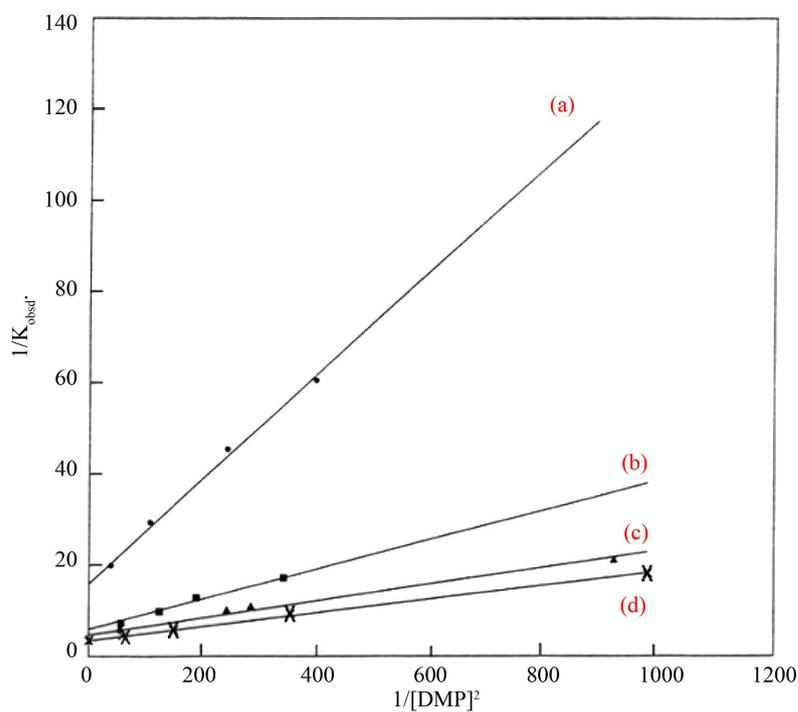


Figure 12. Dependence of the observed pseudo-first order rate constant ($1/k_{\text{obsd}}$) on the $\{1/[\text{DMP}]^2\}$ for the reaction with $[(\text{Pip})_8\text{Cu}_4\text{Cl}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 25°C (a, ●), 38°C (b, ■), 45°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.

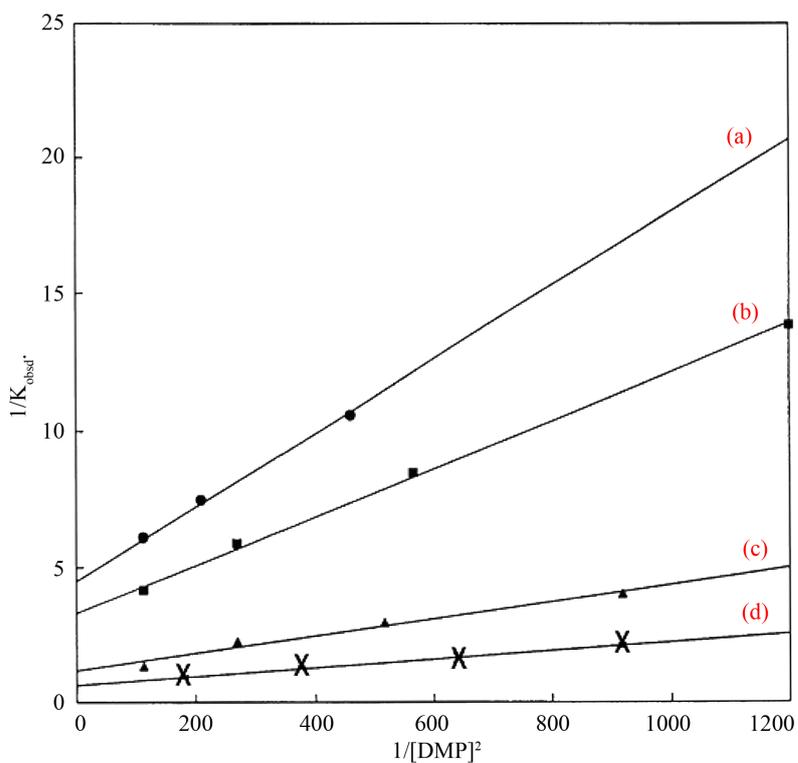


Figure 13. Dependence of the observed pseudo-first order rate constant ($1/k_{\text{obsd}}$) on the $\{1/[\text{DMP}]^2\}$ for the reaction with $[(\text{Pip})_8\text{Cu}_4\text{Br}_4(\text{CO}_3)_2]$, 1.0×10^{-3} M, in $\text{C}_6\text{H}_5\text{NO}_2$ at 20°C (a, ●), 25°C (b, ■), 40°C (c, ▲) and 50°C (d, ×). Monitoring wavelength is 740 nm.

Table 1. Kinetic and thermodynamic parameters for oxidation of (DMP) by [(Pip)_{4n}Cu₄X₄Y₂]; n = 1 or 2, X = Cl or Br and Y = O²⁻ or CO₃²⁻, in C₆H₅NO₂ at 740 nm.

[(Pip) _{4n} Cu ₄ X ₄ Y ₂] n, X, Y	Temp. °C	k ₂ ^{a,b}	ΔH ^{‡c}	ΔS ^{‡d}	K ^e	ΔH ^{°c}	ΔS ^{°d}
2, Cl, O [°]	18	0.170	16.5 ± 0.5	-116 ± 3	3440	13.4 ± 0.5	-86 ± 3
	30	0.260			3800		
	36	0.440			8760		
	42	0.770			9100		
1, Cl, CO ₃	25	0.015	11.2 ± 0.5	-30 ± 3	62	12.0 ± 0.5	-10 ± 3
	32	0.018			78		
	38	0.040			104		
	50	0.062			380		
1, Br, CO ₃	22	0.192	11.0 ± 0.5	-26 ± 3	430	4.0 ± 0.5	-32 ± 3
	28	0.263			540		
	36	0.510			560		
	45	0.770			1040		
2, Cl, CO ₃	25	0.067	12.0 ± 0.5	-23 ± 3	120	3.0 ± 0.5	-39 ± 3
	38	0.167			176		
	45	0.213			196		
	50	0.263			250		
2, Br, CO ₃	20	0.210	12.0 ± 0.5	-22 ± 3	323	0.4 ± 0.5	-46 ± 3
	25	0.310			333		
	40	0.870			357		
	50	1.72			375		

*Previously published data [29] [30].

^aUnits are sec⁻¹. ^bUncertainties for k₂ ca. ± 5% sec⁻¹. ^cUnits are Kcal·mol⁻¹. ^dUnits are cal deg⁻¹·mol⁻¹. ^eUncertainties for K ca. ± 5%.

rate determining step as observed before for the oxo analogues [29] [30]. When the number of piperidine per each Cu changes from one to two, (*i.e.* for [(Pip)_{4n}Cu₄X₄(CO₃)₂]), the mode of coordination of the carbonato-moiety changes from structure **a** to structure **b** (**scheme 2**), such a change let ΔH[°] to decrease from 12 to 3 Kcal·mol⁻¹, when X = Cl and from 4.40 to 0.36 Kcal·mol⁻¹, when X = Br, while ΔS[°] are directed to more negative values for both halo ligands. Therefore, the efficiency of structure **b**, (bidentate carbonato), as an initiator is higher than structure **a**, (tridentate carbonato). On comparing the data for [(Pip)_{4n}Cu₄Cl₄(CO₃)₂]; n = 1 or 2, with [(Pip)₈Cu₄Cl₄O₂] (**Table 1**) where copper (II) centres in all of them are six coordinate, therefore the only difference is oxo versus carbonato, either structure **a** or **b**, (**scheme 2**). In case of oxo, k₂ is at least higher by about factor of 10 and K is higher by a factor of ~50, while ΔH[‡] and ΔH[°] are more endothermic and also ΔS[‡] and ΔS[°] are getting more negative. This indicate that the oxo bridging centre let the catalyst, [(Pip)₈Cu₄Cl₄O₂], more efficient to initiate the cycle than the less basic, more steric carbonato initiators [(Pip)_{4n}Cu₄Cl₄(CO₃)₂] in either structure **a** (n = 1) or **b** (n = 2).

4. Conclusion

Novel complexes of [(Pip)_{4n}Cu₄X₄(CO₃)₂] can be used as initiators for the oxidation of DMP to DPQ, Equation (5). Formation of [(Pip)_{4n}Cu₄X₄(CO₃)₂] complexes suggested that, the Cu-O-Cu angle in [(Pip)_{4n}Cu₄X₄O₂] is sharp to an extent enough to let oxo centre be sufficiently basic for catalytic activity and to ease CO₂ insertion to give the carbonato complexes. On the basis of k₂, K and their kinetic and thermodynamic parameters for the first catalytic cycle, the [(Pip)_{4n}Cu₄X₄(CO₃)₂] are less powerful initiators for oxidative coupling reactions when

compared to $[(\text{Pip})_4\text{Cu}_4\text{X}_4\text{O}_2]$. The above result was attributed to less basic, more steric carbonato moiety relative to the oxo analogue. However, the final yield of the overall catalytic cycles was about the same.

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